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多穗金粟兰中一个新的酚苷*

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摘要：从多穗金粟兰（*Chloranthus multistachys*）全株的甲醇提取物中分离得到1个新的酚苷，通过波谱技术鉴定其结构为丁香酸-4-*O*-α-L-鼠李吡喃糖苷（**1**）。同时还首次从该植物中分离得到两个已知倍半萜内酯和一个已知木脂素：1β，4β-二羟基-5α，8β-二氢-7（11）*Z*-桉叶烯-8，12-内酯（**2**），1β，4α-二羟基-5α，8β-二氢-7（11）Z-桉叶烯-8，12-内酯（**3**），(－)-(7*S*，8*R*)-dihydrodehydrodiconifery alcohol（**4**）。

关键词：多穗金粟兰；金粟兰科；酚苷；倍半萜内酯
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A New Phenolic Glycoside from *Chloranthus multistachys* (Chloranthaceae)

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Abstract: A new phenolic glycoside, named syringic acid-4-*O*-α-L-rhamnopyranoside (**1**), together with three known compounds were isolated from the MeOH extract of the whole plants of *Chloranthus multistachys*. Their structures were elucidated on the basis of extensive spectroscopic. To the best of our knowledge, the three known compounds, 1β, 4β-dihydroxy-5α, 8β(*H*)-eudesm-7(11)*Z*-en-8, 12-olide (**2**), 1β, 4α-dihydroxy-5α, 8β(*H*)-eudesm-7(11)*Z*-en-8, 12-olide (**3**), and (－)-(7*S*,8*R*)-dihydrodehydrodiconifery alcohol (**4**) were all isolated from this plant for the first time.

Key words: *Chloranthus multistachys*; Chloranthaceae; Phenolic glycoside; Sesquiterpene lactones

The plants of genus *Chloranthus* (Chloranthaceae), comprising 15 species, are mainly distributed in the east of Asia (Zhou, 1993). Most of these plants have been using as important medicinal herbs for the treatment of tumors, rheumatisms, and emmeniopathy in traditional Chinese medicine (Jiangsu New Medical College, 1977). Previous phytochemical investigation on this genus revealed the presence of monoterpenoids, sesquiterpenoids, bisesquiterpenoids, diterpenoids, ligans, and flavone glycosides (Wu *et al.*, 2007; Yang and Yue, 2006; Yang *et al.*, 2007; 2008; Wang *et al.*, 2008; Xu *et al.*, 2007; Li *et al.*, 2008). *Chloranthus multistachys* is a perennial herb

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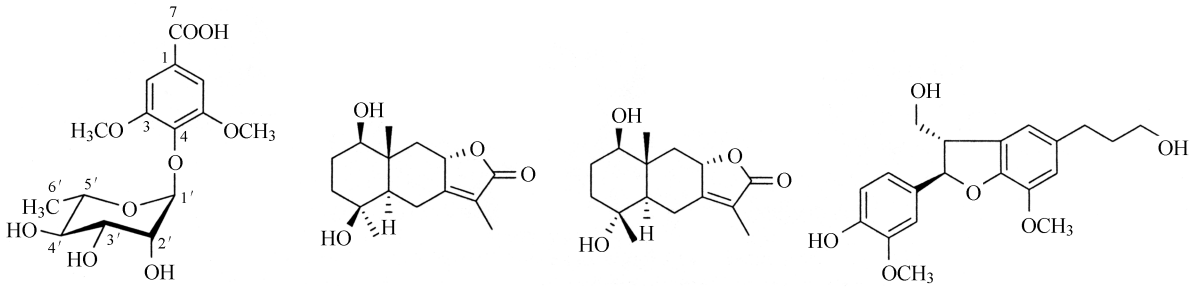
which mainly distributes over the south of China and its roots has been used to treat bone fracture in China as folk medicine (Editorial Committee of the Administration Bureau of Tranditional Chinese Medicine, 1998). One sesquiterpenoid, three bisesquiterpenoids, and nine *ent*-kaurane diterpenoids have been isolated from this plant (Yang and Yue, 2006; 2008). As a part of our systematic research works on the genus (Teng *et al.*, 2009), the chemical constituents of *C. multistachys* were investigated and a new phenolic glycoside, syringic acid-4-*O*-α-L-rhamnopyranoside (**1**) was obtained, along with three known compounds, 1β, 4β-dihydroxy-5α, 8β(*H*)-eudesm-7 (11) *Z*-en-8, 12-olide (**2**) (Yang *et al.*, 2007), 1β, 4α-dihydroxy-5α, 8β(*H*)-eudesm-7 (11) *Z*-en-8, 12-olide (**3**) (Yang *et al.*, 2007), and (−)-(7*S*,8*R*)-dihydrodehydrodiconifery alcohol (**4**) (Zhu *et al.*, 2008) (Fig. 1). In this paper, we report the isolation and structural elucidation of the new phenolic glycoside.



1 **2** **3** **4**

Fig. 1 Structures of compounds **1-4**

Results and Discussion

Compound **1** was isolated as an amorphous powder and showed the molecular formula $C_{15}H_{19}O_9$, with 6 degrees of unsatuation, by the negative HR-ESI-MS at *m/z* 343.1040 [M-H]$^-$. The IR spectrum displayed peaks indicating hydroxygen groups (3422 cm^{-1}), benzene rings (1592, 1502, 1460 cm^{-1}), and carboxyl groups (1700 cm^{-1}). UV absorptions at λ_{max} 211, 254 nm suggested that **1** had an excellent conjugated system. Analysis of the ^{13}C-NMR and DEPT spectra (Table 1) of **1** indicated one carbonyl (δ_C 169.6, s), two methoxyls (δ_C 56.5, q), two sp^2 methines (δ_C 107.7, d), and four sp^2 quaternary carbons [δ_C 128.0 (s), 154.4 (× 2, s), 139.7 (s)], which showed the presence of syringic acid moiety in this compound (Shao *et al.*, 2008). The signals at δ_H 5.33 (d, H-1′), 4.14 (m, H-2′), 3.89 (m, H-3′), 3.44 (m, H-4′), 4.25 (m, H-5′), 1.20 (d, H-6′) in the ^{1}H-NMR spectrum and signals at δ_C 103.3 (d, C-1′), 71.9 (d, C-2′), 72.1 (d, C-3′), 73.6 (d, C-4′), 71.2 (d, C-5′), 17.8 (q, C-6′) in the ^{13}C-NMR spectrum (Table 1) of **1** showed a L-rhamnose in this compound. The anomeric configuration of the rhamnopyranosyl was determined as α-oriented on the ground the chemical shift values of the C-3′ (δ_C 72.1) and C-5′ (δ_C 71.2) to those of the corresponding carbons of methyl α-and β-rhamnopyranoside (Kasai *et al.*, 1979). The L-rhamnose was linked to C-4 by the HMBC correlation from H-1′ to C-4 as shown in Fig. 2. Based on above mentioned evidence, the structure of **1** was identified to be syringic acid -4-*O*-α-L-rhamnopyranoside.

Experimental

General experimental procedures Optical rotation were taken on a Horiba SEAP-300 polarimeter. UV spectra were obtained on a Shimadzu UV-2401PC spectrophotometer. IR spectra were measured with a Bio-Rad FTS-

Table 1　^{1}H and ^{13}C NMR data of compound **1** in CD_3OD (400 MHz and 100 MHz, δ in ppm)

No.	δ_H (Multiplicity, J in Hz)	δ_C	HMBC (H→C)
1		128.0 (s)	
2, 6	7.33 (2H, s)	107.7 (d)	C-1, 3, 7, 4
3, 5		154.4 (s)	
4		139.7 (s)	
7		169.6 (s)	
1′	5.33 (1H, d, 1.7)	103.3 (d)	C-2′, 4′
2′	4.14 (1H, dd, 1.7, 3.3)	71.9 (d)	C-4′, 1′
3′	3.89 (1H, dd, 3.3, 9.6)	72.1 (d)	C-4′
4′	3.44 (1H, t, 9.6)	73.6 (d)	C-3′, 6′
5′	4.25 (1H, m)	71.2 (d)	C-1′, 4′, 6′
6′	1.20 (3H, d, 6.3)	17.8 (q)	C-4′, 5′
3, 5-OMe	3.87 (6H, s)	56.5 (q)	C-3, 5

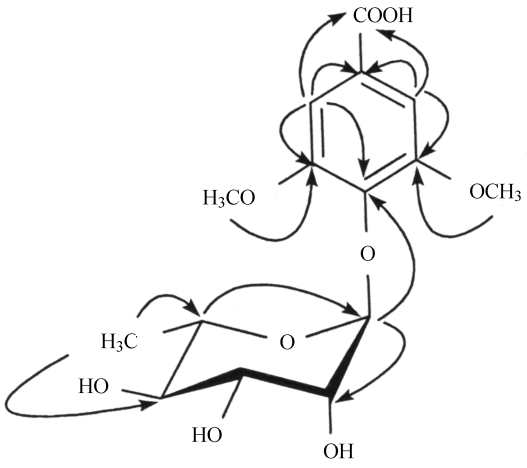


Fig. 2　Key HMBC Correlations of compound **1**

135 spectrometer with KBr pellets. FAB mass spectra were obtained on a VG Auto spec-3000 spectrometer and high-resolution ESI mass spectra were recorded on an API Qstar Pulsar LC/TOF instrument. NMR spectra were measured in CD_3OD and recorded on a Bruker AM-400 or a DRX-500 NMR spectrometer with TMS as an internal standard. Separation and purification were performed by column chromatography on silica gel (200－300 mesh, Qingdao Marine Chemical Inc., Qingdao, People′s Republic of China), RP-18 (Merck), and Sephadex LH-20 (Amersham Biosciences, Sweden). Fractions were monitored by TLC, and spots were visualized by heating silica gel plates sprayed with 10% H_2SO_4 in EtOH.

Plant material　The whole plants *Chloranthus multistachys* was collected in August 2007 from Xinning, Hunan Province, P. R. China, and identified by Dr. En-De Liu of Kunming Institute of Botany. A voucher specimen (No. HY0001) was deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China.

Extraction and isolation　Dried and powered whole plants of *C. multistachys* (20 kg) were extracted three times with CH_3OH under reflux. The filtrate was evaporated under reduced pressure to give a residue, which was suspended into water and partitioned with EtOAc. The EtOAc portion (1300 g) was subjected to column chromatography over silica gel eluted with petroleum ether-Me_2CO (1∶0→1∶1) to give fraction Fr. 1－7. Fr. 3 (50 g) was repeatedly separated on silica gel, Rp-18, and Sephadex LH-20 (MeOH) column chromatography to afford **2** (19 mg), **3** (40 mg), and **4** (30 mg). Fr. 6 (45 g) was chromatographed on silica gel column eluting with $CHCl_3$-MeOH (30∶1→1∶1) and Rp-18 column eluting with a MeOH-H_2O gradient system (20%→60%), further purified on Sephadex LH-20 using MeOH as solvent to yield **1** (15 mg).

syringic acid-4-*O*-α-L-rhamnopyranoside (1): $C_{15}H_{19}O_9$, yellow amorphous powder. $[\alpha]_D^{26} = -81.20°$ ($c = 0.12$, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3422, 2936, 2851, 1700, 1592, 1553, 1502, 1460, 1393, 1129. UV (CH_3OH) λ_{max} (log ε): 211 (4.38), 254 (3.89) nm. ^{1}H-NMR and ^{13}C-NMR: see Table 1. Negative FAB-MS *m/z* (%): 343 [M-1]$^-$ (83), 325 [M-18]$^-$ (100), 197 [M-H-146]$^-$ (43); HR-ESI-MS *m/z*: 343.1040 [M-1]$^-$ (calcd for $C_{15}H_{18}O_9$ cald. 343.1029).

1β, 4β-dihydroxy-5α, 8β (*H*)-eudesm-7 (11)*Z*-en-8, 12-olide (2): $C_{15}H_{22}O_4$, white powder. ^{1}H-NMR (500 MHz, CD_3OD): δ_H 4.94 (1H, m, H-8), 3.24 (1H, dd, J = 3.8, 11.9 Hz, H-1), 2.92 (1H, dd, J = 3.5, 14.1 Hz, H-6α), 2.64 (1H, dd, J = 6.3, 11.8 Hz, H-9β), 2.54 (1H, t, J = 13.6 Hz, H-6β), 1.90 (1H, m, H-2β), 1.81 (3H, m, H-13), 1.72

(1H, m, H-3β), 1.55 (1H, m, H-2α), 1.46 (1H, m, H-3α), 1.23 (3H, s, H-15), 1.20 (3H, s, H-14), 1.16 (1H, dd, J =3.5, 13.1 Hz, H-5), 0.89 (1H, t, J =11.7 Hz, H-9α); ^{13}C-NMR (125 MHz, CD_3OD): δ_C 79.1 (d, C-1), 27.2 (t, C-2), 40.1 (t, C-3), 71.6 (s, C-4), 52.6 (d, C-5), 24.0 (t, C-6), 166.4 (s, C-7), 80.4 (d, C-8), 47.2 (t, C-9), 41.5 (s, C-10), 120.3 (s, C-11), 177.3 (s, C-12), 8.0 (q, C-13), 13.4 (q, C-14), 29.7 (q, C-15).

1β, 4α-dihydroxy-5α, 8β (*H*) -eudesm-7 (11) *Z*-en-8, 12-olide (3): $C_{15}H_{22}O_4$, white powder. ^{1}H-NMR (500 MHz, CD_3OD): δ_H 4.66 (1H, dd, J =6.3, 10.4 Hz, H-8), 3.15 (1H, dd, J =4.3, 11.3 Hz, H-1), 2.96 (1H, dd, J =3.3, 13.9 Hz, H-6α), 2.55 (1H, dd, J =6.2, 11.9 Hz, H-9β), 2.12 (1H, m, H-6β), 1.74 (1H, m, H-3α), 1.68 (3H, s, H-13), 1.57 (2H, m, H-2), 1.48 (1H, m, H-3α), 1.19 (1H, dd, J =13.2, 3.4 Hz, H-5), 1.07 (3H, s, H-15), 0.91 (3H, s, H-14), 0.80 (1H, t, J =11.7 Hz, H-9α); ^{13}C-NMR (125 MHz, CD_3OD): δ_C 77.3 (d, C-1), 27.7 (t, C-2), 40.1 (t, C-3), 71.9 (s, C-4), 53.0 (d, C-5), 22.4 (t, C-6), 163.7 (s, C-7), 78.4 (d, C-8), 46.8 (t, C-9), 39.9 (s, C-10), 119.4 (s, C-11), 175.7 (s, C-12), 7.6 (q, C-13), 13.0 (q, C-14), 21.6 (q, C-15).

(-) - (7*S*, 8*R*) -dihydrodehydrodiconifery alcohol (4): $C_{20}H_{24}O_6$, colorless oil. ^{1}H-NMR (CD_3OD, 400 MHz): δ_H 6.94 (1H, d, J =1.8, H-2), 6.82 (1H, dd, J =1.8, 8.1 Hz, H-6), 6.78 (1H, s), 6.75 (1H, s, H-2′), 6.72 (1H, s, H-6′), 5.49 (1H, d, J =6.3 Hz, H-7), 3.84 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 3.75 (1H, m, H-9), 3.56 (2H, t, J =6.5 Hz, H-9′), 3.46 (1H, m, H-8), 2.62 (2H, t, J =7.4 Hz, H-7′), 1.83 (2H, m, H-8′); ^{13}C-NMR (CD_3OD, 100 MHz): δ_C 134.8 (C-1), 110.5 (C-2), 147.5 (C-3), 145.2 (C-4), 116.1 (C-5), 119.7 (C-6), 89.0 (C-7), 55.4 (C-8), 64.9 (C-9), 136.9 (C-1′), 114.0 (C-2′), 145.2 (C-3′), 149.1 (C-4′), 129.8 (C-5′), 117.9 (C-6′), 35.8 (C-7′), 32.9 (C-8′), 62.2 (C-9′), 56.3, 56.7 (3, 3′-OCH_3).

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